

## Short communication

Ionic liquid as a solvent and catalyst for acylation of maltodextrin<sup>☆</sup>Atanu Biswas<sup>\*</sup>, R.L. Shogren, J.L. Willett

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## ARTICLE INFO

## Article history:

Received 30 December 2008

Received in revised form 10 February 2009

Accepted 12 February 2009

## Keywords:

Ionic liquid

Starch

Maltodextrin

Vinyl stearate

Stearic acid

Esterification

## ABSTRACT

Catalyst-free esterification of maltodextrin was carried out in ionic liquid. Stearate esters of maltodextrin were obtained in various degree of substitution (DS) when vinyl stearate or stearic acid was heated with maltodextrin in ionic liquid, 1-butyl-3-methylimidazolium dicyanamide (bmim[dca]). Reaction temperature of 75 °C gave the highest value of DS (0.64) and reaction efficiency (64%). Structure and DS of the resulting esters were confirmed by NMR, titration, GC, and elemental analysis. It was found that for some of the maltodextrin stearates the mixed solvent of chloroform/DMSO (70/30) was better than DMSO.

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## 1. Introduction

Among the industrial materials, starch is one of the cheapest and most cost-effective. In addition to being a major food item, it is currently used industrially as coatings and sizing in papers, textiles and carpets, as binders and adhesives, as absorbants, and as encapsulants (Whistler and BeMiller, 1993; Stephen, 1995). Starch has been modified to expand its uses for a variety of industrial applications. The properties of modified starch can be altered extensively through variation in the chemical nature of the derivative and DS. For example, esterification of the hydroxyl group to provide DS of 1.5–3.0 can impart thermoplasticity and water resistance to the starch, compared to the unmodified starch.

Hydrolysis of starch (Wang and Wang, 2000) produces a group of low-molecular-weight carbohydrates named dextrans. Dextrans are mixtures of linear and branched  $\alpha$ -(1,4)-linked D-glucose polymers. They have the same general formula as amylose but are of shorter chain length. Dextrans find widespread use in industry, due to their non-toxicity and low price. They are used as water soluble glues, as thickening agents in food processing, and as binding agents in pharmaceuticals. In pyrotechnics, they are added to colored fire formulas, allowing them to solidify as pellets or “stars”. Cyclodex-

trins find additional use in analytical chemistry as a matrix for the separation of hydrophobic substances, and as excipients in pharmaceutical formulations (Shimpi et al., 2005). Not all forms of dextrin are digestible, and indigestible dextrin is sometimes used as fiber supplements.

Derivatization of starch and other polysaccharides with hydrophobic groups (Mahil and Glass, 2003; Kapusniak and Siemion, 2007) confers important properties such as surface activity, water resistance, and self-association, leading to higher solution viscosity and self-organization into nanoparticles. Applications include emulsifiers, water resistant coatings, rheology modifiers and drug delivery. Alkenylsuccinate esters of starch have been studied (Trubiano, 1986) extensively and are commonly used at low DS levels as emulsifiers in food.

Starch stearates would have potential in the above applications but previous preparation methods involve expensive reagents or catalysts. For examples, starch stearates have been prepared using fatty acid chlorides and anhydrides, but these reagents are rather expensive. Other authors have utilized lipases (Rajan and Abhraham, 2006; Rajan et al., 2006, 2008) to catalyze the transesterification of starch and vinyl stearate. The drawbacks include the high cost of the enzyme, the need to form starch nanoparticles first, or the need for solvents such as DMSO or DMF which can be difficult to separate from the modified starch. Thus, there is an opportunity to develop an alternative method for the preparation of starch stearates which is less expensive.

In this work, we found an inert solvent 1-butyl-3-methylimidazolium dicyanamide (bmim[dca]) for maltodextrans that also catalyzed the esterification reaction with vinyl stearate or stearic acid, Fig. 1. This would enable us to improve the starch

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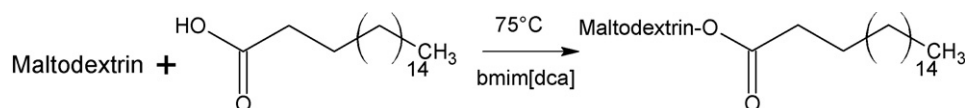


Fig. 1. Reaction between maltodextrin and stearic acid.

or dextrin properties by modifying them with many reactants that would have been difficult otherwise. The ionic liquid was extracted with ethanol after the reaction and can presumably be recycled and reused.

## 2. Experimental

### 2.1. Chemicals and instrumentation

Maltodextrin (Star Dri-1) was obtained from A. E. Staley (now Tate & Lyle), Decatur, IL. Ionic liquid (bmim[dca]), Fig. 2, was prepared by following the procedure outlined in the work of Sheldon (Liu et al., 2006). Spectrapor membrane tubing was obtained from Thermo Fisher.  $\text{CDCl}_3$  and  $d_6$ -DMSO were obtained from Cambridge Isotope. All other chemicals were obtained from Aldrich. NMR spectra in  $\text{CDCl}_3$  were obtained by using Bruker Instrument DRX 400 spectrometer. Elemental analyses were done by Galbraith Laboratories Incorporated, Knoxville, TN.

### 2.2. Synthesis of starch stearate in DMSO

Maltodextrin (Star Dri-1) 0.5 g (3 mmol) and 8.32 g (8 ml) of ionic liquid bmim[dca] were mixed and heated to 90 °C for 30 min. To this solution, 0.96 g (3 mmol) of vinyl stearate or 0.85 g of stearic acid (0.3 mmol) was added. The reaction was conducted in an incubator shaker for ~65 h at 75 °C, 200 rpm. The reaction was suspended in ethanol to remove free vinyl stearate and centrifuged at 3400 rpm for 10 min. The pellet was then washed three additional times in ethyl alcohol. The residual pellets were suspended in 50 ml water and heated to 90 °C in order to dissolve as much of the starch into solution as possible. The samples were dialyzed with Spectrapor® membrane tubing, molecular weight cut off 6000–8000 to remove any residual ionic liquid for four full days of dialyzing, with twice a day water changes. The samples were then centrifuged at 3400 rpm for 10 min before the supernatant was freeze dried (A). The residual pellet was suspended in ethanol and centrifuged at 3400 rpm for 10 min. The supernatant was discarded and pellets were dried in the vacuum oven at 50 °C for a couple of days (B). Recovery yields were determined by combining both dried A and B portions. Degree of substitution (DS) was determined by proton NMR (Fig. 3).

### 2.3. Degree of substitution

The DS of the starch stearate was determined by  $^1\text{H}$  NMR using the ratio of the 1/28 of 28 methylene proton absorbance at 1.2–1.4 divided by 1/7 of the total starch CH areas, i.e. at 3.2–3.9 (6H) and 5.2 (1H) ppm.

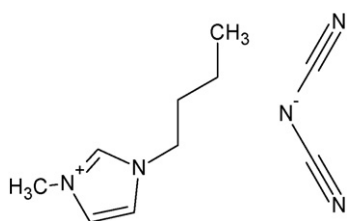


Fig. 2. Chemical structure of ionic liquid bmim[dca].

## 3. Results and discussion

The limited solubility of polysaccharides restricts the number and nature of reagents that could be used for their modification. Starch is only soluble in limited number of solvents, such as water and DMSO. However, the reactive nature of DMSO precludes many reagents that could have been used to modify starch. It has been reported (Liu et al., 2006) that starch is soluble at room temperature in ionic liquid, bmim[dca]. However, the viscosity becomes so high that it was difficult to stir the solution. We found that maltodextrin is highly soluble in bmim[dca] and we used 6% solution to react with vinyl stearate. One advantage with bmim[dca] is that it is liquid at room temperature.

As shown in Table 1, starch stearates prepared at 40 °C had very low (<0.01) DS and consequently were mostly water soluble. Even the use of Novozym 435 lipase did not affect the reaction at 40 °C (data not shown). At 55 °C, the values of DS increased slightly to 0.024 and water solubility was maintained. The addition of Novozym 435 gave a small but significant increase in DS over the control at 55 °C. The enzyme was likely denatured in the presence of bmim[dca], in agreement with previous studies. Increasing temperature to 75 °C gave a dramatic increase in DS to 0.63. The reason for this large increase in DS with temperature is uncertain but may be due to an increase in solubility of vinyl stearate in bmim[dca] at higher temperature. Vinyl Stearate has a melting point at about 70 °C. Below 70 °C, it is a solid and has lower reactivity. Above 70 °C, stearate melts to a liquid. It is reasonable that a liquid reaction gives a higher yield of the product than a solid reaction. This starch stearate had very low solubility in water or DMSO (Dona et al., 2007) but was soluble in the mixed solvent,  $\text{CDCl}_3/\text{DMSO}$  at 70/30 weight ratio.

Using stearic acid instead of vinyl stearate gave approximately equal weights of a low DS (0.06) water soluble starch stearate and a high DS (0.64) fraction that was insoluble in water but soluble in DMSO at 90 °C. For the stearic acid reaction, a vacuum of 7 Torr was applied to remove water of condensation. The starch stearate was washed with diethyl ether to remove any unreacted stearic acid or vinyl stearate, collected the washings and evaporated the volatiles. We found only (~1%) of stearic acid was extracted, indicating that stearate was covalently bound. This represents the

Table 1

Preparation of maltodextrin stearates in bmim[dca] using 0.5 g Star Dri-1 and 0.96 g vinyl stearate.

Temperature (°C)	Water soluble (A)		Water insoluble (B)	
	DS <sup>a</sup>	Yield (%) <sup>b</sup>	DS <sup>a</sup>	Yield (%) <sup>b</sup>
1. 40	0.003 ± 0.000	95	0.008 ± 0.001	1
2. 55	0.024 ± 0.001	95	0.039 ± 0.015	1
3. 55 <sup>c</sup>	0.035 ± 0.002	88	0.059 ± 0.012	3
4. 75	0.63 ± 0.209	9	0.63 ± 0.184	210 <sup>d</sup>
5. 75 <sup>e</sup>	0.06 ± 0.012	68	0.64 ± 0.061	73

<sup>a</sup> Determined using  $^1\text{H}$  NMR. Conditions were  $\text{DMSO}-d_6$  at 70 °C except for #4 which was  $\text{CDCl}_3/\text{DMSO}-d_6$  at 23 °C.

<sup>b</sup> Yield based on weight of starch.

<sup>c</sup> 0.1 g Novozym 435 lipase added.

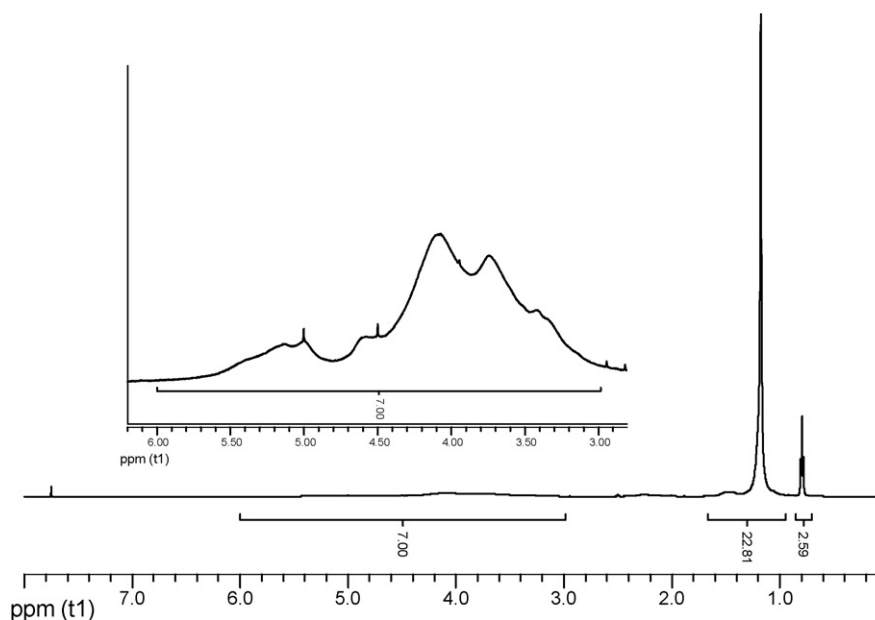
<sup>d</sup> The yields are over 100% because they are based on starch weight, not the weight of starch + vinyl stearate. The maximum yield should be 260% based on 0.5 g starch, 0.96 g vinyl stearate and accounting for loss of weight of acetaldehyde.

<sup>e</sup> 0.85 g stearic acid added instead of vinyl stearate; vacuum of 7 Torr applied.

**Table 2**

Comparison of methods used to characterize DS of starch steirates prepared at 75 °C.

Reactant	Water soluble/insoluble portion	DS via methods				
		NMR		Filtration	GC	CHO analysis
		DMSO	70%CDCl <sub>3</sub> /30%DMSO			
Vinyl stearate	Soluble	1.62	0.656		0.652	0.63
Vinyl stearate	Insoluble	2.94	0.852	0.85		0.85
Stearic acid	Soluble	0.068			0.068	0.03
Stearic acid	Insoluble	0.713				0.72

**Fig. 3.** Proton NMR of starch stearate 4 (DS 0.63), in CHCl<sub>3</sub>/DMSO 70/30.

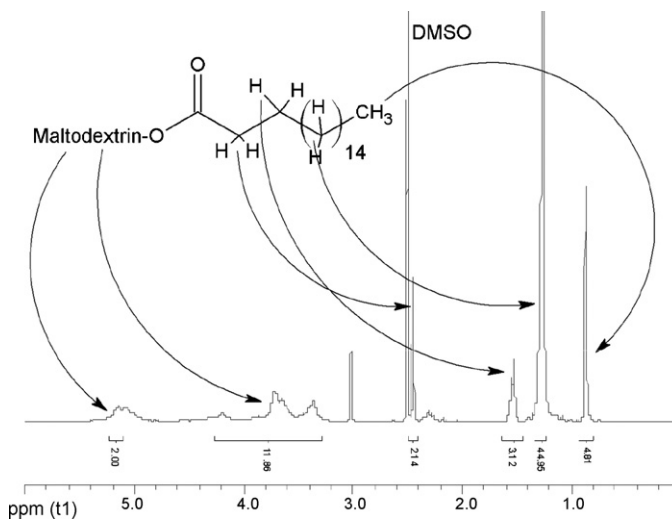
first report of preparation of a starch stearate by direct esterification of starch with stearic acid. The fact that such a reaction occurs at all at such mild temperature is rather remarkable since most esterifications require much higher temperatures or strong acid catalysts. This suggests that the ionic liquid bmim[dca] is also acting as a catalyst. Indeed, when other ionic liquids were used such as 1-butyl-3-methylimidazolium chloride as solvent, esterification did not proceed. Thus, the basic nature of dicyanamide anion appears to play a key role in catalyzing the esterification process.

The structure and composition of the steirates were confirmed by NMR, by base hydrolysis and weighing of released stearic acid, by methylation and GC and by elemental analysis. Most previous studies have characterized DS of starch steirates by <sup>1</sup>H NMR in DMSO at elevated temperatures. We found, however, that this method gave highly variable and impossibly high results for starch steirates of intermediate DS (Table 2). For example, the maximum DS was 1.0 based on the amount of vinyl stearate added while values of 1.6–2.9 were determined in DMSO-*d*<sub>6</sub> at 70 °C.

It was subsequently discovered that CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub> gave much clearer solution for product of reaction 4 (DS 0.63) and these results agreed well with DS determinations by hydrolysis and weighing stearic acid released, by GC of methyl esters and by elemental (C, H & O) analysis.

The starch stearate made with stearic acid was soluble in DMSO but the one made with vinyl stearate was not soluble in DMSO even though DS values were similar. This may indicate a different substitution pattern or perhaps the acetaldehyde released may react with starch to change solubility. The solu-

bilities of vinyl stearate and stearic acid in bmim[dca] may also be a factor. The proton NMR of sample 4 in chloroform/DMSO is shown in Fig. 3. Fig. 4 shows the NMR of sample 5 in DMSO. Even though both of these samples have about same DS of about 0.6, sample 4 made from vinyl stearate was soluble in mixed solvent system of chloroform/DMSO (70/30) whereas sample 5 made from stearic acid dissolved readily in DMSO only.

**Fig. 4.** Proton NMR of starch stearate 5 (DS 0.64), in DMSO.

Interestingly, some of the starch stearate samples (#4) swollen in toluene showed reflection of blue light suggesting they had liquid crystalline properties. In addition, the blue color disappeared upon heating to 50 °C indicating that such materials are temperature responsive. More work is being carried out in this area and will be reported in due course.

This study has shown that starch stearates of a range of DS and solubilities can be prepared simply by heating starch, ionic liquid bmim[dca] and an acyl donor. Most previous preparation methods have required use of vinyl stearate as well as a harsh chemical or enzymatic catalyst. The ability to use cheap stearic acid rather than the much more expensive vinyl stearate may help to make such novel starch esters more practical. Some applications for these materials may include coatings, emulsifiers, dispersing agents and nanoparticles.

#### 4. Conclusions

Maltodextrin is soluble in ionic liquid 1-butyl-3-methylimidazolium dicyanamide in high concentration. We have found that at 75 °C maltodextrin in bmim[dca] reacted with stearic acid or vinyl stearate to give maltodextrin stearate with DS of 0.60 in good yields. No enzyme or any other catalysts was required for this process. In this work we have demonstrated that ionic liquid could simultaneously act as a solvent and catalyst for reaction between maltodextrin and vinyl ester or fatty acid.

#### Acknowledgements

The authors would like to thank Kelly Utt and Janet Berfield for their excellent technical assistance.

#### References

- Dona, A., Yuen, C.W., Peate, J., Gilbert, R.G., Castignolles, P., Gaborieau, M., 2007. A new NMR method for directly monitoring and quantifying the dissolution kinetics of starch in DMSO. *Carbohydr. Res.* 342 (17), 2604–2610.
- Kapusniak, J., Siemion, P., 2007. Thermal reactions of starch with long-chain unsaturated fatty acids. *J. Food Eng.* 78, 323–332.
- Liu, Q., Janssen, H.A., Rantwijk, F.V., Sheldon, R.A., 2006. Room-temperature ionic liquids that dissolve carbohydrates in high concentrations. *Green Chem.* 7, 39–42.
- Mahil, D.M., Glass, J.E., 2003. Hydrophobically-modified, water-soluble polymers: commercially important polymer additives. *Polym. Mater.: Sci. Eng.* 89, 639.
- Rajan, A., Abhraham, T.E., 2006. Enzymatic modification of cassava starch by bacterial lipase. *Bioprocess Biosyst. Eng.*, 65–71.
- Rajan, A., Prasad, V.S., Abhraham, T.E., 2006. Enzymatic esterification of starch using recovered coconut oil. *Int. J. Biol. Mac.* 39, 265–272.
- Rajan, A., Sudha, J.D., Abhraham, T.E., 2008. Enzymatic modification of cassava starch by fungal lipase. *Ind. Crops Prod.* 27, 50–59.
- Shimpi, S., Chauhan, B., Shimpi, P., 2005. Cyclodextrins: application in different routes of drug administration. *Acta Pharm.* 55, 139–156.
- Stephen, A.M. (Ed.), 1995. *Food Polysaccharides and their Applications*. Dekker, New York, Basel, Hong Kong.
- Trubiano, P.C., 1986. Succinate & substituted succinate derivatives of starch. In: Wurzburg, O.B. (Ed.), *Modified Starches: Properties and Uses*. CRC Press, Boca Raton, FL, pp. 136–143.
- Wang, Y.J., Wang, Y., 2000. Structures and properties of commercial maltodextrins from corn, potato, and rice starches. *Starch* 52 (8/9), 296–304.
- Whistler, R.L., BeMiller, J.N. (Eds.), 1993. *Industrial Polysaccharides and their Uses*, 3rd ed. Academic Press, San Diego.